E(MP2)[CH_3CO^-] = −152.864 142 hartree. As mentioned above, E(MP2)[CH_3CO] = −152.860 509 hartree so the acetyl ion is now predicted to be bound, with respect to CH_3CO and a free electron, by 3.6 mhartree or 0.1 eV. Instead of subtracting the total energies of the anion and radical, one might use Koopmans' approximation[40] to estimate the electron affinity. Use of the highest occupied orbital for CH_3CO^-, $\psi_{12}(a')$ with eigenvalue $\epsilon_{12} = -0.0448$, leads to a "frozen orbital" EA ≅ 1.2 eV. These theoretical estimates should be compared with our experimental finding of EA(CH_3CO) = 0.423 ± 0.037 eV.

Conclusions

The results of our experimental findings are summarized in Table IV and Figure 5. Our ab initio calculations are collected together in Tables V and VI and are entirely congruent with our experimental results.

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Registry No. CH_3CO^-, 78944-68-0; DCH_2CO^-, 121141-79-5; CH_3CO, 3170-69-2; DCH_2CO, 121141-80-8; $(CH_3)_3SiCOCH_3$, 13411-48-8; F^-, 16984-48-8; $CH_2DCOSi(CH_3)_3$, 121141-81-9; $H_2C{=}CHOCH_3$, 107-25-5; $ClSi(CH_3)_3$, 75-77-4; $H_2C{=}C(OCH_3)Si(CH_3)_3$, 79678-01-6; D_2O, 7789-20-0.

SERRS of Langmuir–Blodgett Monolayers: Spatial Spectroscopic Tuning

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Abstract: Surface-enhanced resonance Raman scattering (SERRS) is shown to be a unique tool to perform selective analytical spectroscopy of a specific layer in a bilayer sample without apparent interference from adjacent material. The spatial spectroscopic tuning was achieved on Langmuir–Blodgett monolayers of two different molecules with electronic absorption in the visible. Since the surface Raman electromagnetic enhancement extends well beyond the first adsorbed monolayer, it is possible for the SERRS of upper layers to be much stronger than the surface-enhanced Raman scattering (SERS) signal from the first monolayer deposited onto a Ag surface. The SERS active surface was of Ag-coated Sn spheres that have been shown to be good enhancing surfaces in a wide spectral region encompassing that of the Ag and Au island films.

The interest in the structure and characterization of Langmuir–Blodgett (LB) monolayer film assemblies continues to grow in view of their wide scope of applications, especially in the field of molecular electronics.[1,2] For monomolecular layers or mixed layers with submonolayer concentrations, molecular sensitive analytical techniques are needed to study, for instance, chemical reactions[3] in LB monolayers and changes due to interactions at the interface. Surface-enhanced Raman spectroscopy[4] and, in particular, SERRS[5,6] provide both molecular specificity and sensitivity for monolayer and submonolayer quantities.[7,8] There are alternative ways in which the sensitivity of the inelastic scattering can be improved to be applied to the study of thin monolayer assemblies, for example, waveguide Raman scattering[9] (WRS) or simply resonant Raman scattering.[10] However, it is shown here that SERRS is a unique nondestructive method for selective vibrational characterization of monolayers and submonolayer film assemblies. By tuning into molecular resonances and plasmon resonances[11] of the enhancing surfaces and using the fact that there exists electromagnetic enhancement at a distance above the surface (up to ca. 10 nm), the spectral properties of specific components in multilayers and/or mixed-layer assemblies could be probed. The feasibility of this spectroscopic tuning is demonstrated here for LB monolayers of two molecular dyes with strong electronic absorption in the visible.

Experimental Section

Langmuir–Blodgett monolayers of $(t\text{-Bu})_4$VOPc and N, octyl-substituted 3,4:9,10-perylenebis(dicarboximide) {Oc-PTCDNH} (see Figure 1) were prepared at room temperature and transferred to Corning 7059 glass slides or slides with Ag-coated Sn spheres in a Lauda trough equipped with an electronically controlled film deposition device. Monolayers were compressed at a speed of 0.1 A^2/molecule/s, and the film transfer was carried out at 4.8 mm/min at a pressure of 10 dynes/cm. Monolayers were transferred by substrate withdrawal (or Z-type deposition). For spreading onto the water surface the $(t\text{-Bu})_4$VOPc and the Oc-NPTCNH were dissolved in toluene. Ag-coated Sn spheres[12] were formed by evaporating 100 nm mass thickness of Sn at a rate of 0.5 nm/s onto glass substrate heated at 120 °C. An amount of 100 nm of Ag was then overlaid with the substrate held at room temperature. The 514.5-, 568.2-, and 647.1-nm lines of the Ar^+ and Kr^+ ion laser were used with a typical power of 100 mW. Raman shifts were measured with a Spex-1403 and a Ramanor-1000 double monochromator (with micro-

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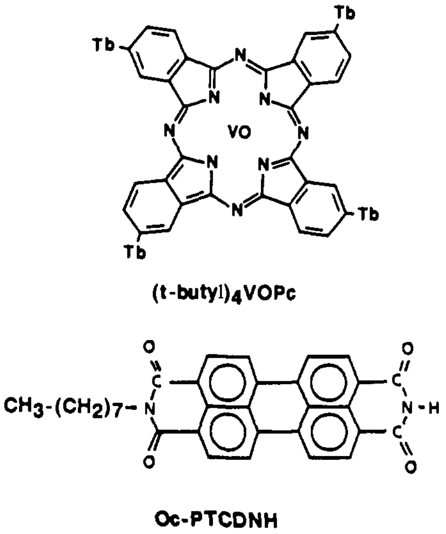

Figure 1. Chemical structures of the phthalocyanine and perylene derivatives used for LB studies.

scope attachment for back-scattering geometry) with a typical band-pass of 5 cm^{-1}.

Results and Discussion

A partial vibrational assignment of observed infrared (IR) and Raman frequencies and characterization of the (t-Bu)$_4$VOPc LB monolayers has been previously reported.[13] It was found that IR spectra, the Raman scattering (RS), and the RRS spectra were dominated by the vibrational frequencies of the parent Pc molecule. This is in agreement with the well-known fact that the Raman cross sections of molecular vibrations associated with a conjugated system are much larger than those of saturated groups. The most prominent features in the spectra were (as in most Pc molecules) the macrocycle vibrations at 685 and 754 cm^{-1} and the pyrrole stretching vibrations at 1330 and 1523 cm^{-1}. The 754-cm^{-1} band was characteristic of resonant Raman spectra. Fundamental vibrational frequencies of LB layers on Ag-coated Sn spheres were observed unshifted from their values in the spectra of the bulk, an indication of physisorption, as opposed to chemisorption, of the Pc molecules on the metal surface. The SERRS effect did not alter the pattern of relative intensities observed for the vibrational fundamentals in the molecular RRS. The synthesis of Oc-PTCDNH was reported by Nagao et al.,[14] who kindly provided the sample for the present work. The vibrational spectra of Oc-PTCDNH monolayers were similar to what was observed for PTCDI molecule,[15] with strong Raman bands 1292, 1379, and 1572 cm^{-1}. A complete vibrational characterization of a series of perylenebis(dicarboximide)s is presently carried out in our laboratory.

The 647.1-nm Kr$^+$ laser line is in resonance with the red absorption band of (t-Bu)$_4$VOPc, and the 514.5-nm line of the Ar$^+$ laser is in resonance with the main absorption maximum of the Oc-PTCDNH, while the 568.2-nm line is in the preresonance region of the Pc molecule. Therefore, excitation with the 647.1-nm line of, for instance, a mixture of both molecular dyes would give the spontaneous Raman spectrum of the Oc-PTCDNH and the resonant Raman spectrum of (t-Bu)$_4$VOPc or SERS and SERRS in the case of surface-enhanced effect. The opposite holds for excitation with the 514.5-nm laser line. Since SERRS would give rise to a signal to noise ratio at least 2 orders of magnitude higher than SERS, a selective spectroscopic identification of the component in the mixture can be attained by tuning into the appropriate molecular resonance.[12]

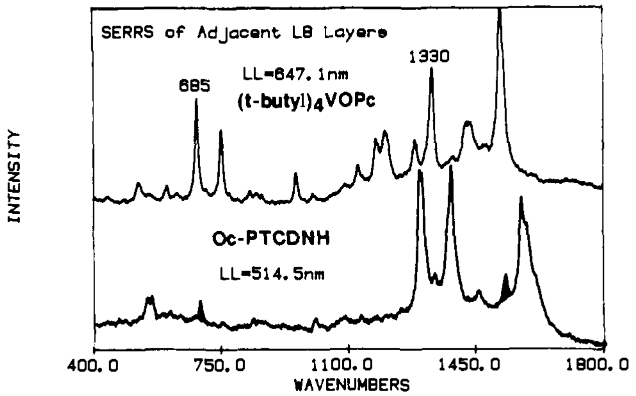

Figure 2. SERRS from sample A (Ag/Oc-PTCDNH/Pc) under two different excitation wavelengths.

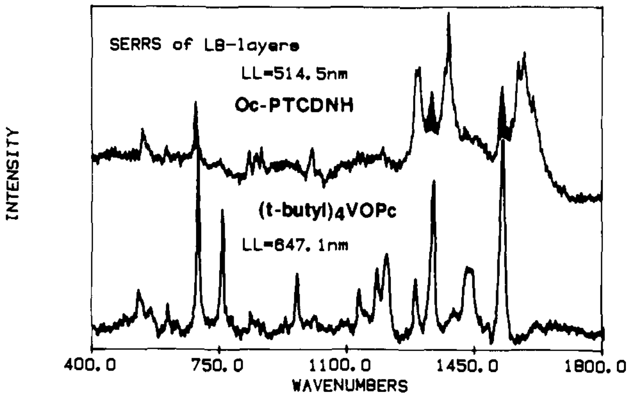

Figure 3. SERRS from sample B (Ag/Pc/Oc-PTCDNH). Pc bands in the SERRS spectrum of Oc-PTCDNH are shown with shaded area.

In Figure 2, the bottom spectrum was obtained for a sample A, which consisted of a Oc-PTCDNH LB monolayer deposited onto Ag-coated Sn spheres (the SERS active surface), and covered with one LB monolayer of (t-Bu)$_4$VOPc. Since the 514.5-nm exciting line was in resonance with the molecular absorption of Oc-PTCDNH, the fundamental vibrations of this molecule dominated the spectrum, and it should be labeled SERRS of Oc-PTCDNH. The upper traces in the same figure were obtained for the same sample A but under 647.1-nm excitation, showing that SERRS signals of the upper LB layer of (t-Bu)$_4$VOPc were stronger than the SERS signals from the Oc-PTCDNH layer directly attached to the metal surface. Since the upper layer was obviously detached from the Ag surface, the strong SERRS signal is due to electromagnetic enhancement, which has been shown to extend far out the surface.[16] Clearly, the spectroscopic tuning was possible due to the fact that SERRS at a distance is stronger than the SERS of the monolayer directly attached to the Ag surface.

A second sample was prepared (sample B), where the LB monolayers were deposited onto the Ag-coated Sn spheres in the reverse order. The recorded spectra are presented in Figure 3. The lower trace was obtained with 647.1-nm laser line, given the SERRS of (t-Bu)$_4$VOPc monolayer directly physisorbed onto the Ag. By tuning into the molecular resonance of Oc-PTCDNH (514.5 nm) the vibrational spectrum of the second layer becomes dominant, indicating once again that the SERRS of Oc-PTCDNH at a distance was also stronger than the SERS from the (t-Bu)$_4$VOPc monolayer located in the immediate vicinity of the Ag surface. For laser lines that are not within the main absorption of one of the two molecular resonances, the spatial spectroscopic tuning would not be possible, and spectra with strong vibrational fundamental from both layers could be observed. For example, in Figure 4 the spectrum of sample A obtained with the 568.2-nm

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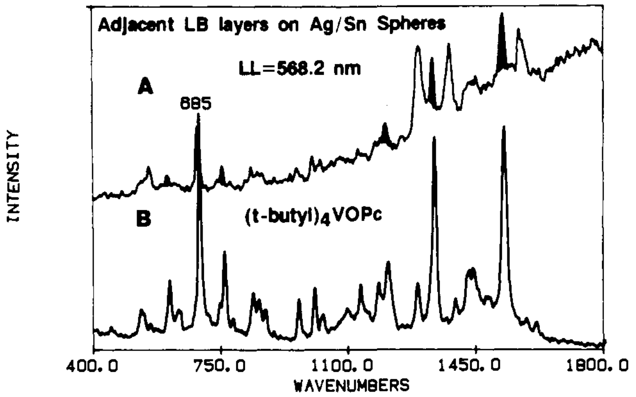

Figure 4. Raman shifts from samples A and B obtained with 568.2-nm laser line.

laser line is shown, where both the vibrational fundamentals of the bottom layer (Oc-PTCDNH) and the upper monolayer of (t-Bu)$_4$VOPc contribute to the Raman spectrum. The sample B with the reverse order of LB layers, under 568.2-nm excitation, gave the spectrum of (t-Bu)$_4$VOPc. This result was in agreement with the fact that 568.2-nm was in preresonance region of the Pc electronic transition, but it was outside of the absorption region of Oc-PTCDNH.

Conclusion

The application of SERRS in the spatial spectroscopic analysis of adjacent LB monolayers has been demonstrated using molecular dyes with distinct electronic absorption in the visible. The spatial spectroscopic tuning may be used to study a variety of sequential monomolecular assemblies, for instance, to follow the interaction and spectral changes in separate monolayers containing donor and acceptor species or a chemical binding (reaction) that could affect one specific layer. In general, SERRS could be used for selective spectroscopic analysis of an LB monolayer in a matrix of spacers of molecules transparent to the exciting electromagnetic field.

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Dioxygen Adsorption on Well-Outgassed and Partially Reduced Cerium Oxide Studied by FT-IR

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Abstract: $^{16}O_2$ ($^{18}O_2$) adsorption on well-outgassed and partially reduced cerium oxide has been investigated by Fourier transform infrared spectroscopy (FT-IR) in the temperature range 200–373 K. Superoxide species ($O_2^-{}_{ads}$) with a pair of characteristic bands at 1126 (1063) and 2237 (2112) cm^{-1} were detected from oxygen adsorption on both surfaces of well-outgassed and partially reduced cerium oxide. One additional band at 883 (835) cm^{-1} attributed to peroxide species ($O_2^{2-}{}_{ads}$) was observed together with the bands at 1129 and 2238 cm^{-1} after oxygen adsorption on partially reduced cerium oxide. The formation of these dioxygen species is strongly dependent on the pretreatment of cerium oxide. In particular, the bands due to peroxide species were only identified on the partially reduced cerium oxide, and the band intensities increased markedly with the prereduction time of cerium oxide. It is concluded that the superoxide species is mainly generated on a coordinatively unsaturated cerium ion while the peroxide species were formed on a pair of surface cerium ions with lower oxidation state created by reduction.

Identification of dioxygen species on surfaces of metals and oxides has long been an attractive subject[1] because the dioxygen species are the most essential intermediates of many heterogeneous oxidation reactions,[2] which consist of the basis for important industrial processes, such as production of oxygen-containing compounds through selective oxidation. Although oxygen adsorption on transition-metal oxides has been extensively examined, the ways how these species form and participate in reactions are still obscure. A detailed study on dioxygen species is therefore necessary for understanding the oxidation mechanism on oxides. Cerium oxide, a rare-earth oxide, has been found to be active for oxidation reactions of hydrocarbons[3,4] and CO.[5,6] The studies of adsorbed oxygen species and their activities on cerium oxide have drawn some attention; for example, ESR (electron spin resonance) investigations[7,8] show that superoxide species, O_2^-, were formed on CeO_2 and on supported CeO_2 with certain pretreatments after oxygen adsorption. Che et al.[9,10] assumed that the O_2^- species adsorbs on Ce^{3+} ion of cerium oxide based on the ESR spectra. O_2^- species were also confirmed[11] on CeO_2/Al_2O_3 and CeO_2Pd/Al_2O_3, and the species were proved to be the active form on the latter during the oxidation reaction of CO and C_2H_4. All above conclusions related to the oxygen species on cerium oxide were drawn only on the basis of ESR results. No IR study of O_2 adsorption on cerium oxide has been reported; especially, no evidence of adsorbed O_2^{2-} species has been obtained for cerium oxide. We reported preliminary oxygen adsorption on ceria by means of IR method.[12]

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